

ELECTROCHEMICAL DEVICE FOR ENVIRONMENTAL SAFETY MONITORING

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The electrochemical behavior of porous titanium and copper structures in the phosphoric acid, containing ions Cu^{2+} , was studied. The conditions of the corrosion resistance of the electrode materials were established. As a result of the researches a three-electrode amperometric device for determining sulfur dioxide in the air was developed. Device contains gas-diffusion catalytically active platinized titanium electrode as a working electrode and a copper reference electrode. The laboratory test of the developed devices was carried out and metrological characteristics were established. In the range of measured concentrations, resolution, speed and stability of characteristics, the developed device corresponds to the sensors that are included in unified series of Igor Sikorsky Kyiv Polytechnic Institute.

Intensification of economic and industrial activity of man in modern terms of nature and extent of human impact on the main components of the biosphere created the situation of environmental crisis at the beginning of the new millennium. Particularly acute is the problem of air pollution with various harmful substances. One of the most common ecotoxicants is sulfur dioxide (SO_2). The toxic properties of sulfur dioxide consist in a sharp irritation of respiratory organs and mucous membranes of the eyes. Especially strongly toxic properties of sulfur dioxide manifest themselves by prolonged fogs and the formation of smog. In this case, sulfur dioxide causes an aggravation of diseases of the upper respiratory tract and leads to an increase in mortality in large cities. For instance, in London, from poisoning of SO_2 ($\sim 4.5 \text{ mg/m}^3$) within 5 days, more than 4000 people died, and up to 10 thousand people became seriously ill [1]. Sulfur dioxide is the most phytotoxic among the technogenic emissions. The effect of sulfur dioxide on plants is mainly caused by the products of its transformation in atmospheric air, primarily sulfuric acid, which falls in the form of acid precipitation, the so-called "acid rain".

According to the statistics of the Ministry of Ecology and Natural Resources of Ukraine for the period from 2005 to 2013, in Ukraine, the atmosphere was annually affected by 1200...1300 thousand tons of sulfur dioxide [2]. At the same time there is a tendency to increase

emissions, which is due to the replacement of natural gas with coal in fuel and energy balances. It should be noted that in the coal produced in Ukraine, the sulfur content is very high – from 1.7 to 3.6 % [3]. Therefore, in Ukraine, thermal power plants account for almost 80 % of sulfur dioxide emissions.

To determine the concentration of SO₂ in various analyzed media, a wide range of methods and means of measurement are used. Among the variety of devices, electrochemical sensors have an advantage [4]. For the determination of SO₂, voltammetric [5-8], potentiometric [9], much less frequently coulometric [10] and conductometric [11] sensors are used. Each of them has a number of restrictions on the application. In the coulometric and conductometric SO₂ sensors, absorbing solutions containing oxidants are used, most often I₂. Such devices are marked by impressive dimensions, low selectivity and limited operating period, prolonged analysis procedure. To determine SO₂, high-temperature potentiometric sensors based on solid electrolytes with alkali and alkaline earth metal sulfates, sodium rare earth silicates, lead, zirconium oxides, are used. Due to the high operating temperature (500...1300 °C) and the use of a platinum indicator electrode, the sum of all reducing gases is finally determined, which makes it impossible to analyze complex mixtures [9].

Research methodology

As a current-conducting base of the electrodes, a titanium powder of fraction 0.05...0.1 mm was used. Catalytically active coatings on a titanium base were obtained by thermal decomposition of the corresponding metal salts. Investigation of the electrochemical behavior of electrode materials was carried out in the potentiostatic regime on electrodes with a diameter of 18 and a thickness of up to 1 mm, made in the form of thin-layer structures pressed onto the fluoroplastic rigid substrate at an effort of 360 MPa. The values of the potentials in the work are given relative to the normal hydrogen electrode.

Electrochemical cells of the devices were made by layer pressing of functional layers. The counter electrode (1) and the reference electrode (2) were placed in the same plane (Fig. 1, a). The electrodes were separated by separators (3), which included silica gel and fluoroplastic powder in a weight ratio of 1:2.

The working electrode of the cell, which contained 0.1 g of platinized titanium (5) (50 mg Pt per 1 g Ti), was pressed onto a titanium layer (4) (0.2 g). The thickness of the working electrode was about 0.25 mm. The overall dimensions of the electrode with a porosity of 30% allow the electrochemical reaction to proceed at the interface of the three phases "gas – electrolyte – catalytically active coating". The counter electrode of the cell contained 0.1 g of titanium activated with ruthenium dioxide (150 mg RuO₂ per 1 g Ti), and the reference electrode was 0.1 g copper

powder. After fabrication, impregnation with a solution of 52% phosphoric acid with the addition of 0.1 mol/l CuSO_4 and removal of excess electrolyte solution from the cell surface by filter paper, it was mounted in the plastic

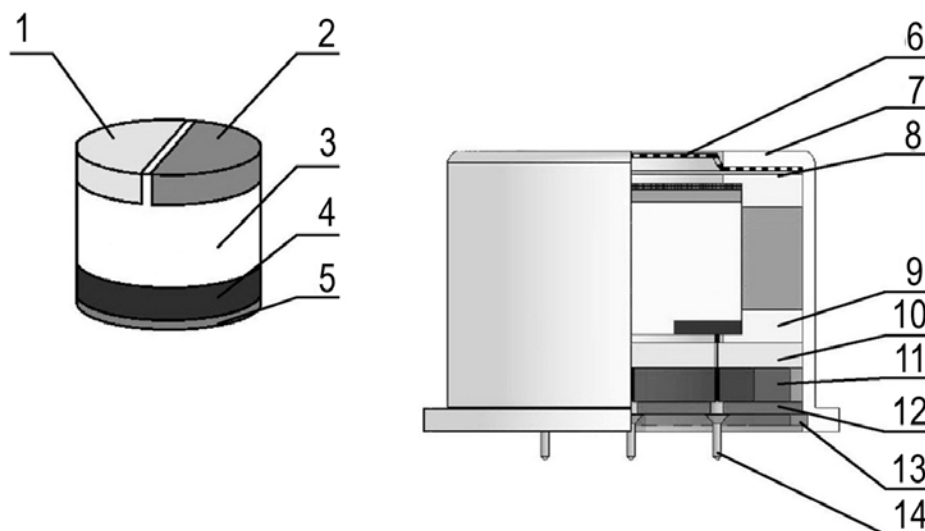
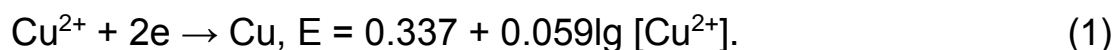


Fig. 1. Electrochemical cell (a) and the structure of the three-electrode device (b). 1 – dioxide-ruthenium counter electrode; 2 – reference copper electrode; 3 – diaphragm; 4 – titanium sublayer; 5 – titanium-platinum working electrode; 6 – metal protective mesh; 7 – case; 8 – diffuse porous diaphragm; 9 – polyethylene holder; 10 – dielectric disk; 11 – rubber ring; 12 – mounting plate; 13 – lock ring; 14 – pin.

case of the unified sensor series (Fig. 3, b). The electrochemical device was connected by means of flexible conductors to the measuring complex, which consisted of a potentiostat PI-50-1, a programmer PR-8, a two-coordinate potentiometer PDA-1-01. The tests were carried out on a static micro-dosing unit with a capacity of 20 liters. The electrochemical device was connected with a potentiostat with flexible conductors and placed in a container.

Results and Discussion

The behavior of porous titanium electrodes in 52 and 78 % solutions of phosphoric acid with addition of Cu^{2+} ions was studied by recording the change in the electrode potential in time (Figures 2, 3). The initial potentials of titanium porous electrodes in both pure phosphoric acid and in the presence of Cu^{2+} ions are close. But in the presence of Cu^{2+} ions the potential is shifted to the cathode side for 10...20 hours with subsequent stabilization in the range 0.29...0.35 V, which corresponds to the flow of the electrode process



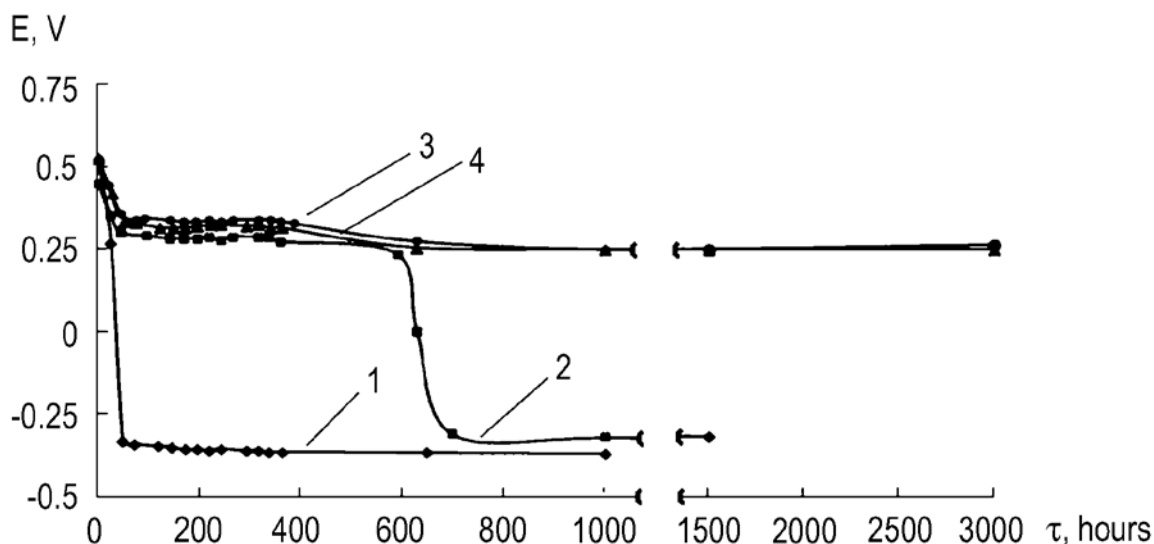


Fig. 2. Change in time of the non-current potential of a porous titanium electrode in 50 % H₃PO₄ with the addition of copper ions, mol/l: 1– 0; 2– 0.025; 3 – 0.1; 4 – 0.3.

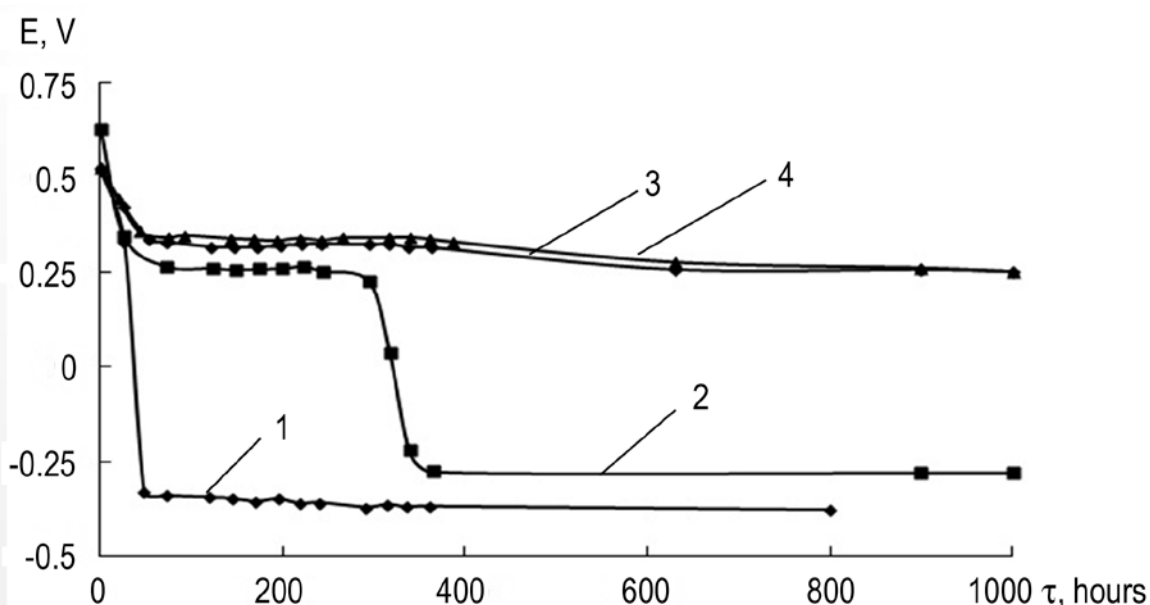


Fig. 3. Change in time of the non-current potential of a porous titanium electrode in 78 % H₃PO₄ with the addition of copper ions, mol/l: 1– 0; 2– 0.025; 3 – 0.1; 4 – 0.3.

This means that a phase precipitate of copper forms on the surface of titanium grains due to contact deposition, which leads to the stabilization of the potential of the porous titanium electrode in the region of passivity of titanium for a long time. The time of transition of titanium to the active state depends, first of all, on the concentration of copper (II) ions and the concentration of phosphoric acid.

Proceeding from the sufficient stability of porous titanium in solutions of phosphoric acid in the presence of copper (II) ions, and based on the

obtained results on the behavior of titanium electrodes with catalytically active coatings, a three-electrode amperometric-type device for determining the sulfur dioxide content is proposed. Platinized titanium was selected as the material of the working electrode, and titanium activated with ruthenium dioxide (75 mg RuO₂ per 1 g Ti) was added to the counter electrode. For the reference electrode, an electrochemical system Cu/Cu²⁺ is chosen, whose electrode reaction is described by the equation (1). Electrolytic copper powder was used as the reference electrode material. As studies have shown, the potential of such an electrode in solutions of phosphoric acid is characterized by sufficient stability (Figure 4). This indicates that the exchange current for reaction (1) is greater than the exchange current of all electrode reactions possible under given conditions.

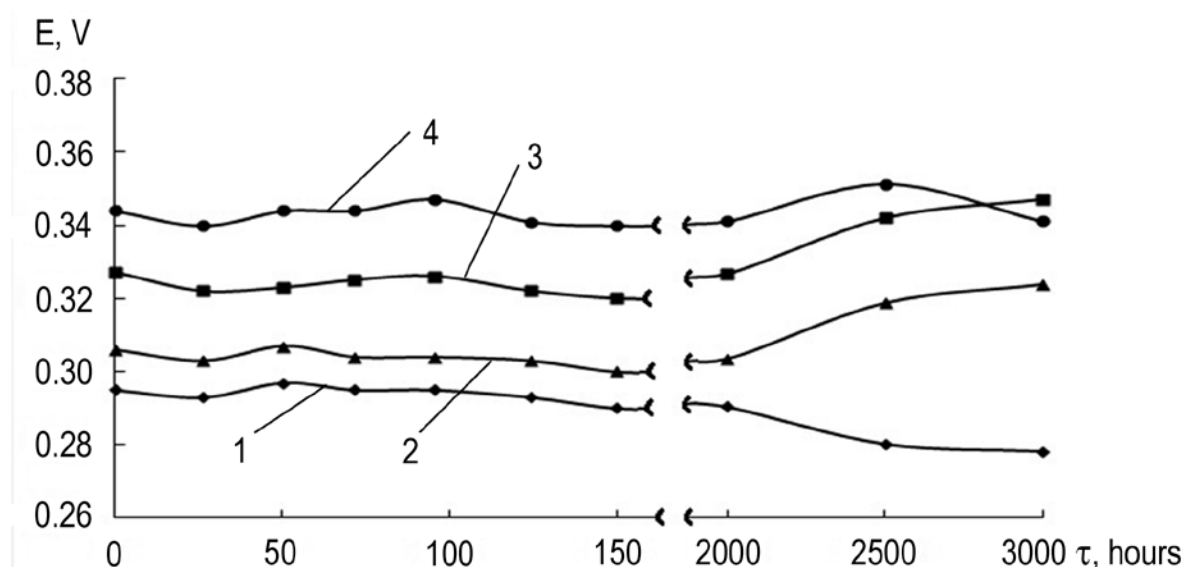
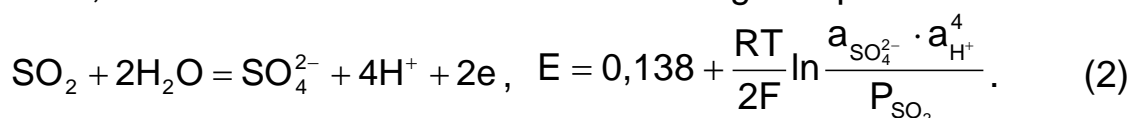


Fig. 4. Change in time of the non-current potential of a porous copper electrode in a solution of H₃PO₄ with a concentration of 10 % (4), 50 % (1, 3), 78 % (2) and with addition of 0.1 mol/l Cu²⁺ (3, 4)

To determine the operating range of the potentials of the developed device, the anodic polarization of the indicator electrode in an air atmosphere in the presence of sulfur dioxide was investigated. Figure 5 shows the anode polarization curves taken with the sweep rate of the potential $5 \cdot 10^{-4}$ V/sec. Such curves approximate in character to stationary ones. As can be seen from the presented curves, the value of current potentials in the presence of SO₂ decreases with increasing concentration of SO₂, but much more theoretically possible equilibrium potentials, which should be established according to equation



The observed significant deviation of the experimental values of E for the electrodes from the equilibrium potentials in the presence of SO_2 is due to the course of the conjugated oxidation reactions of adsorbed SO_2 and the reduction of atmospheric oxygen by reaction



or oxygen adsorbed on the surface of platinum. During the anodic polarization of the working electrode, the flow of current is fixed, the value of which in the first approximation is proportional to the concentration of SO_2 .

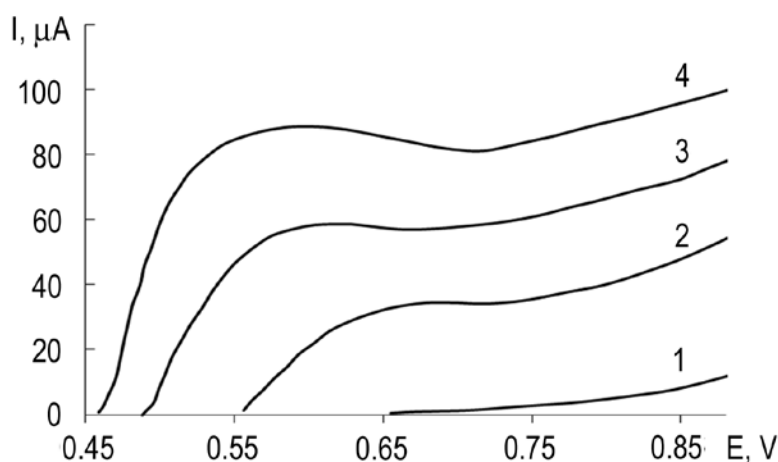


Fig. 5. Anodic polarization curves on a platinized titanium electrode at SO_2 concentration in air, ppm: 1 – 0; 2 – 12; 3 – 21; 4 – 34. The sweep speed of the potential is $5 \cdot 10^{-4}$ V/sec.

The optimal range of potentials for an amperometric sensor is 0.6...0.75 V, in which the oxidation of sulfur dioxide occurs at the limiting current. Current flow at potentials exceeding 0.8 V is associated with the reaction of electrochemical oxygen evolution.

Figure 6 shows the change in the sensor output signal over time with a working electrode potential of 0.65 V at different SO_2 concentrations. The received data testify that the speed of the sensor is less than 60 sec, which corresponds to the level of sensors that are produced serially. The relationship between the output signal of the sensor and the concentration of SO_2 in the range 0–50 ppm is linear. The deviation from linearity with increasing SO_2 concentration and the instability of the output signal (curve 5, Figure 6) are probably related to the processes occurring at the working electrode. They can be represented in the general form by the reaction of the interaction of $\text{SO}_{2\text{ads}}$ adsorbed on the surface of the molecule with the oxygen adsorbed on the electrode surface by equation



with subsequent hydration and desorption of the reaction products.

Surface oxygen concentration is restored due to the oxidation of water on the electrode by equation



At the counter dioxide ruthenium electrode, atmospheric oxygen reduction takes place according to equation (3). Totally on the electrodes the following reaction proceeds

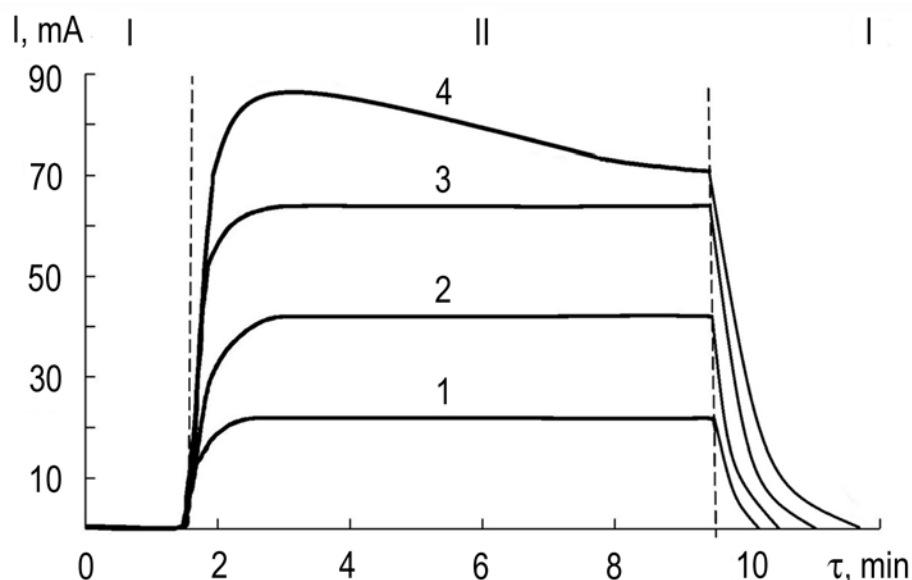


Fig. 6. Change in the output signal of a three-electrode device with a working electrode potential of 0.65 V. Zone: I – air, II – air with addition SO_2 . Concentrations of SO_2 , ppm: 1 – 23; 2 – 45; 3 – 70; 4 – 112.

If the stage of formation of oxygen adsorbed on the surface (5) is slowed down, then the amount of SO_2 delivered to the electrode exceeds the amount of adsorbed oxygen formed. Then part of the surface is blocked by the strongly adsorbed $\text{SO}_{2\text{ads}}$ particles, which leads to further inhibition of the reaction (5).

A series of 8 devices was manufactured, on which the output characteristics were examined once every three months. As the tests showed, the output characteristics of the devices during the year have deviations from the initial values within the limits not exceeding 10 %. This is probably due to the fluctuation of external factors – temperature, relative humidity. Such a deviation lies within the limits of the relative error for gas analytical instruments in accordance with GOST 2603-94.

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Conclusions

The applicability of copper ions as an effective inhibitor of the corrosion processes of porous titanium structures in phosphate acid is shown. It was established that at a concentration of copper ions of 0.05 mol/l for 2500 hours, no signs of titanium corrosion in the investigated solutions of phosphoric acid were observed. The laboratory samples of three-electrode amperometric devices for determination of sulfur dioxide were used, in which platinized titanium was used as the working electrode, the reference electrode was copper, and the electrolyte was a solution of phosphoric acid with the addition of 0.1 M CuSO_4 . It is established that the speed and sensitivity of the developed sensor is comparable with the same characteristics for serial sensors, while the content of platinum is reduced by a factor of 10.

References

- [1] Rovinsky F.Ya., Egorov V.I., Ozone, oxides of nitrogen and sulfur in the lower atmosphere, Gidrometeoizd, 1986.
- [2] <http://www.menr.gov.ua/ekolohichni-pokaznyky-monitorynhu/3829-pokaznyk-a-1>
- [3] Dolgiy V.Ya., Krivchenko AA, Shamalo M.D., The content of total sulfur in coal seams in mines of Ukraine, Coal of Ukraine, 1, P. 10-12, 2000.
- [4] Chviruk V.P., Polyakov S.G., Gerasimenko Y.S., Electrochemical monitoring of technological environments, Academperiodica, 2007.
- [5] Chachulski B., Gebicki J., Analytical characteristics of a new amperometric sulfur dioxide sensor, Chem. anal., 51 (1), P. 135-146, 2006.
- [6] Hodgson A.W., Jacquinet P., Hauser P.C., Electrochemical sensor for the detection of SO_2 in the low-ppb range, Anal. Chem., 71 (14), P. 2831-2837, 1999.
- [7] Shi G., Luo M., Xue J., Xian Y.; Jin L.; Jin J.-Y., The study of PVP/Pd/IrO₂ modified sensor for amperometric determination of sulfur dioxide, Talanta, 55 (2), P. 241-247, 2001.
- [8] Chiou C.-Y., Tse-Chuan Chou T.-C. Amperometric sulfur dioxide sensors using the gold deposited gas-diffusion electrode, Electroanalysis, 8 (12), P. 2279-2282, 1996.
- [9] Fergus J.W., A review of electrolyte and electrode materials for high temperature electrochemical CO_2 and SO_2 gas sensors, Sens. and Actuators. B, 134 (2), P. 1034-1041, 2002.
- [10] Chen G.N., Liu J.S., Duan J.P., Chen H.Q., Coulometric detector based on porous carbon felt working electrode for flow injection analysis, Talanta, 53, P. 651–660, 2000.
- [11] Yu S.G., Yi W., Single-walled carbon nanotubes as a chemical sensor for SO_2 detection, IEEE Trans. Nanotechnol, 6 (5), P. 545-548, 2007.